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Atmospheric corrosion evaluation of electrogalvanized, hot-dip galvanized and galvannealed interstitial free steels using accelerated field and cyclic tests

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ABSTRACT

Three years of outdoor corrosion tests, accelerated with a saline solution spray, and SAE J2334 and GM 9540P accelerated corrosion tests of industrially coated electrogalvanized (GE), hot-dip galvanized (GI), galvanneal (GA) interstitial free steels were performed. The samples were industrially phosphatized and painted with a modified epoxy resin, polyester resin as a primer and a base coat, and a high solid acrylic resin varnish as a clear coat. The effect of the deposition process and zinc mass on atmospheric corrosion of galvanized interstitial free low-alloyed carbon steels was analyzed. The SAE J2334 test was more effective than the GM 9540P test in differentiating the lowest corrosion resistance of the hot dip galvanized steel among the galvanized steels studied. The duration of the accelerated field test played an important role in the steel performance rating. The parameter of maximum corrosion penetration was more efficient to distinguish the effect of the zinc mass on corrosion resistance of the galvanized steel samples evaluated using accelerated field tests.

1. Introduction

The search for galvanized and painted steels with optimized corrosion resistance for use in construction, automotive and home appliance industries has motivated numerous research works [1–9]. The electrogalvanized and galvanneal steels are the two most commonly used materials [10,11]. The latter is gaining more markets due to its low cost and excellent weldability conditions [9].

The automotive paint system has brought innumerable improvements, that apart from the multitude of available colors, higher brightness and paint elasticity, vibrant colors restricted to certain sporting niches invade the popular car segment, such as green and blue that refers to ecology and sustainability. The automotive paint system has also reached a better tribological and chemical resistance [6]. To achieve this performance, the automotive industry has invested in new types of pre-treatment such as γ-mercaptopropyltrimethoxysilane (MTMO) [9]. New inorganic–organic hybrid precursors for corrosion protective coatings on galvanized iron were studied, and three different types of precursor sols, such as pure boehmite, hydrolyzed 3-glycidyloxypropyltrimethoxysilane (GPS), and boehmite–GPS hybrid sols were prepared and deposited on ultrasonically cleaned galvanized iron plates by using a dip coating technique at room temperature [12]. Organic resins such as topcoat based on acrylic resins/polyester/melamine and varnishes formulated with acrylic resin/melamine were developed [13,14]. The incorporation of chromating reagents in an acrylic lacquer applied on galvanneal and galvanized steel was studied by Feliu and Barranco [15].

Zinc alloy coatings have played an important role in improving the corrosion resistance of steels used in automotive, construction and home appliance industries for the last thirty years [1,5]. Zinc coatings act as an adherent barrier layer and as a cathodic protection [4]. Zn based coatings may be obtained by electrodeposition, thermal spraying or immersion in liquid metal baths (hot-dipping) at 450 °C [16,17]. The most common industrial hot-dip (HD) zinc coatings used in Brazil are the GI (Zn–0.2 wt.% Al), galvalume or Al55Zn (55 wt.% Al, 43.5 wt.% Zn, 1.5 wt.% Si), and galvanneal or GA which is obtained by annealing at temperatures from 490 °C to 540 °C [4].

The Zn layer of electrogalvanized and hot-dip (HD) galvanized steels consists of the zeta phase. The galvanneal coating is composed of fragile Fe—Zn intermetallic compounds (IMCs), namely zeta-phase (monoclinic $FeZn_{13}$: 5.8–6.5 wt.% Fe), palisade delta ($FeZn_{10}$: 7.0–8.3 wt.% Fe), compact delta-phase (hexagonal $FeZn_7$: 10.3–11.7 wt.% Fe), gamma-1 (face-centered cubic Fe_5Zn_{21}: 16.3–18.5 wt.% Fe), and gamma (body-centered Fe_3Zn_{10}: 22.2–28.2 wt.% Fe) [18]. The galvanneal coating contains approximately 10 wt.% Fe, and its coating thickness is less than that of the HD galvanized coatings [19]. The alloy coating on galvanneal is typically about 7 μm in thickness [20]. Phase identification of IMCs in galvanneal is crucial and was performed using techniques such as Mossbauer and

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Table 1
Procedure of the SAE J2334 cyclic test.

Stage	Test conditions	Exposure (days of a week)						
		1	2	3	4	5	6	7
1st stage Humid chamber	Relative moisture: >95% Temperature: 50 °C ± 2 °C	6 h	6 h	6 h	6 h	6 h	✗	✗
2nd Stage Salt spray	Saline solution: 0.5% m/v de NaCl + 0.1% wt./v de $CaCl_2$ + 0.075% wt./v de $NaHCO^3$, Room temperature	15 min	15 min	15 min	15 min	15 min	✗	✗
3rd Stage Dry chamber	Relative humidity: 50% ± 5% Temperature: 60 °C ± 2 °C	17 h and 45 min	17 h and 45 min	17 h and 45 min	17 h and 45 min	17 h and 45 min	✗	✗
4th Stage Dry chamber	Relative humidity: <50% ± 5% Temperature: 60 °C ± 2 °C	✗	✗	✗	✗	✗	24 h	24 h

The wet surface period of this test is 18% and the corrosion rate expected is 3.0 kg Fe/m^2 year

Raman spectroscopy [20,21], transmission electron microscopy (TEM) [22], Glow Discharge Optical Emission Spectroscopy (GDOES) [20], and X-ray diffraction (XRD) [23]. IMCs volume fraction distribution defines the coating formability [18] and its main failure mode is the powdering, where particles with a mean size smaller than the coating thickness are produced and powdered [17]. Powdering may be mitigated by controlling the Fe enrichment kinetics during the coating production [18].

Surface chemistry and morphology, alloy composition, phase composition and the deposition process of zinc-iron coatings strongly influence their corrosion resistance [1,24–26]. Specifically, in the automotive industry, hot-dip Zn-based coatings are often applied to interstitial free (IF) steels due to the ductility necessary for deep drawing [27].

Recently, Santos et al. [4] performed a comparative study of the electrochemical behavior of industrially coated hot-dip galvanized and galvanneal steels. However, the atmospheric corrosion behavior of these steels including the electrogalvanized steel, evaluated using the accelerated field test, is scarce in literature. Yadav et al. [28] have investigated the effect of Fe—Zn alloy layers which are formed during the hot-dip galvanizing process on the corrosion resistance of galvanized steel under atmospheric marine environment by using an accelerated wet–dry cyclic corrosion test, potentiodynamic polarization, surface potential measurement, and AC impedance techniques. Silva et al. [29] have also described the corrosion resistance of galvannealed steel under marine atmosphere. Yadav et al. [28] have discussed the role such layers play in enhancing the protective ability of zinc corrosion products considering atmospheric corrosion. A comparative study of atmospheric corrosion resistance of industrially painted electrogalvanized, hot-dip galvanized and galvannealed steels using the accelerate field test with spray of a saline solution and cyclic tests is not found in literature. The effect of the deposition process and the mass of zinc coating on the atmospheric corrosion resistance of galvanized steels is discussed.

The accelerated field test is advantageous mainly for joining a reduced test time, a low cost, and the simulation of the condition in service, exposing the steels to an industrial atmosphere with a saline spray.

2. Material and methods

The cold rolled steels used were interstitial free (IF) ultra-low carbon steel, electrogalvanized (GE) steels, and hot dip galvanized with heat treatment of the zinc layer (GA) and without heat treatment (GI). The substrate of the coated steels was the IF ultra-low carbon steel with a nominal thickness of 0.8 mm. The steel samples were obtained from industrial coils. The values of mass per area of metallic coatings for the GE steel were 45, 55 and 60 g/m^2, for the GI steel were 40, 60 and 80 g/m^2 and for the GA steel were 40 g/m^2 and 60 g/m^2. The values of thickness of the zinc layer were 5.6, 6.3, 7.7, and 8.4 μm for 40, 45, 55, and 60 g/m^2 of zinc mass per area, respectively.

The samples for the corrosion tests with dimensions of 100 mm × 150 mm were processed in a Brazilian automotive industry. The phosphate used was tricationic and the painting consisted of the following steps: electrophoretic painting process with a modified epoxy resin (thickness of 19 ± 1.2 μm), polyester resin as a primer (thickness of 35.0 ± 2.8 μm) and a base coat (thickness of 18.0 ± 0.9 μm), and a high solid acrylic resin varnish as a top coat (thickness of 40.0 ± 3.1 μm). The values of thickness of painting layers are shown in Table 3.

The edges of each specimen as well as the areas containing identification marks were protected by a coating of two-component epoxy polyamide. The paint film on one side of each sample was mechanically scratched by a machining tool with a tungsten carbide tip, which reached the base metal, forming an internal angle of 60° ± 15°. The scratch was made on the sample diagonally. The distance between the end of the scratch and the edge was 20 mm, according to the NBR 8754 Brazilian standard.

The thickness of the dry paint film was measured according to the NBR 10443 standard, and the adhesion was evaluated by using the draw method. The adhesion of the dried paint film was measured affixing pullout pins of 12.7 mm in diameter on the paint surface. The adhesive used was the two-component type: Huntsman Aradur 1012 (aliphatic polyamine) hardener and a DER 383 liquid epoxy resin provided by Dow Plastics (Dow Chemical Company), at a ratio of 35/65 parts of hardener by parts of resin. The pins were detached by

Table 2
Procedure of the GM 9540P accelerated cyclic corrosion test.

Stage		Conditions	
1st Stage	Application of salt spray for 15 min Intervall of 75 min	0.9% wt./v of NaCl + 0.1% wt./v of $CaCl_2$ plus 0.25% wt./v of $NaHCO_3$, pH = 6.0 a 8.0 Wet chamber at 25 °C ± 2 °C without salt spray	Repeated 4 times before the next step
2nd Stage	2 h in wet chamber	25 °C ± 2 °C and relative humidity >30%	
3rd Etapa	8 h in wet chamber	49 °C ± 2 °C and relative humidity between 95% and 100%	
4th Etapa	7 h in dry chamber	60 °C ± 2 °C and relative humidity <30%	
5th Stage	1 h in dry chamber	25 °C ± 2 °C and relative humidity <30%	

Wet surface of the test period is 48% and the corrosion rate expected is 12.0 kg/m2 year

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